INTERMEDIATES TO ETHYLENE GLYCOL:
CARBONYLATION OF FORMALDEHYDE CATALYZED BY NAFION®
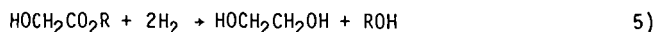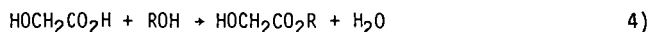SOLID PERFLUOROSULFONIC ACID RESIN
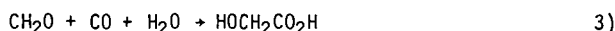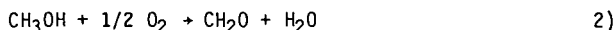
Dan E. Hendriksen

Corporate Research-Science Laboratories
Exxon Research and Engineering Company
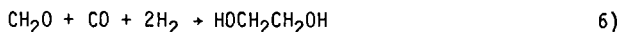P.O. Box 45
Linden, New Jersey 07036

INTRODUCTION

Carbon monoxide and hydrogen can be converted to ethylene glycol by a variety of direct and indirect routes. This work explores an indirect route proceeding through the acid-catalyzed carbonylation of formaldehyde, using a novel strong acid catalyst, Nafion solid perfluorosulfonic acid resin. The glycolic acid product of this carbonylation may be esterified and then hydrogenated to yield ethylene glycol. Ethylene is presently the feedstock for ethylene glycol production; the ethylene is partially oxidized to ethylene oxide,[1a] which is then hydrolyzed to yield ethylene glycol.
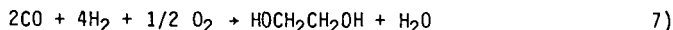
In this work, the following sequence of reactions is envisioned.

$$CO + 2H_2 \rightarrow CH_3OH \qquad\qquad 1)$$

$$CH_3OH + 1/2\ O_2 \rightarrow CH_2O + H_2O \qquad\qquad 2)$$

$$CH_2O + CO + H_2O \rightarrow HOCH_2CO_2H \qquad\qquad 3)$$

$$HOCH_2CO_2H + ROH \rightarrow HOCH_2CO_2R + H_2O \qquad\qquad 4)$$

$$HOCH_2CO_2R + 2H_2 \rightarrow HOCH_2CH_2OH + ROH \qquad\qquad 5)$$

Equations 3, 4, and 5 may be combined to yield equation 6,

$$CH_2O + CO + 2H_2 \rightarrow HOCH_2CH_2OH \qquad\qquad 6)$$

and the sum of equations 1 - 5 is equation 7.

$$2CO + 4H_2 + 1/2\ O_2 \rightarrow HOCH_2CH_2OH + H_2O \qquad\qquad 7)$$

In this sequence, equations 1 and 2 are the conventional processes for methanol[1b] and formaldehyde[1c] production, respectively. Both are high volume chemicals whose production technology is well-developed. The remaining transformation desired, starting with formaldehyde, is shown as equation 6. This is accomplished through the carbonylation of formaldehyde to yield glycolic acid, as shown in equation 3, followed by the esterification of this acid, equation 4, and the hydrogenolysis of the ester to ethylene glycol, equation 5.

The overall reaction from carbon monoxide and hydrogen, equation 7, is instructive since it reveals that this process essentially couples two reactions, the direct synthesis of ethylene glycol from CO/H_2, equation 8,

$$2CO + 3H_2 \rightarrow HOCH_2CH_2OH \qquad\qquad 8)$$

and the burning of hydrogen, equation 9.

$$H_2 + 1/2\ O_2 \rightarrow H_2O \qquad\qquad 9)$$

While conversion to ethylene glycol is severely limited by the unfavorable thermodynamics of the direct synthesis, equation 8, the coupling of this reaction with the highly exothermic equation 9 results in a sequence in which the high-energy intermediate formaldehyde may be quantitatively converted to ethylene glycol with no thermodynamic constraints.

It is well known that strong acids catalyze the carbonylation of formaldehyde to yield glycolic acid. Solid acid catalysts for this reaction have been explored to some extent, but there is only a single example in the patent literature of catalysis by Nafion®. In this case, the carbonylation of formaldehyde was carried out in acetic acid solvent to yield acetylglycolic acid.[2] The present work significantly extends the reaction chemistry accessible with this novel acid catalyst.

RESULTS AND DISCUSSION

"Nafion-H" Resin.[a] There are several properties of DuPont's "Nafion-H" perfluorosulfonic acid resin which make it an ideal candidate for the strong acid-catalyzed carbonylation of formaldehyde. First, it is a superacid; i.e., stronger in intrinsic acidity than 100% sulfuric acid. The resin is a copolymer of tetrafluorethylene and perfluoro-3, 6-dioxa-4-methyl-7-octensulfonic acid, resulting in a structure:

$$-(CF_2-CF_2)_n - CF_2 - CF -$$
$$|$$
$$O$$
$$|$$
$$CF_2$$
$$|$$
$$CF - CF_3$$
$$|$$
$$O$$
$$|$$
$$CF_2$$
$$|$$
$$CF_2$$
$$|$$
$$SO_3H$$

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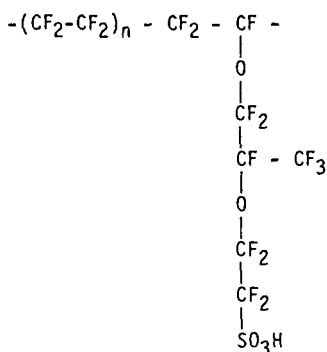
[a]"Nafion-H" is a convenient notation to indicate the acid form of this ion exchange resin. "Nafion" is a registered trademark of DuPont.

By analogy, one might expect the resin to be nearly as acidic as trifluoromethane sulfonic acid, CF_3SO_3H. DuPont claims that its acidity is of the same order as $AlCl_3 \cdot HCl$. Second, the resin is thermally very stable. DuPont states that there should be no problem with deterioration below 175°, and their safety data show significant decomposition only above 270°. Others have found the material to be stable and useful to at least 220°.[3] Third, the resin is swelled by polar organic solvents, allowing reactants to diffuse into the resin granules. This makes the interior acid sites available, as well as the acid sites on the catalyst surface. Furthermore, the resin is chemically inert, being deactivated only by ion exchange with e.g., Fe^{3+}. Such deactivated catalysts are readily regenerated by the same technique used to prepare the acid form of the resin. The resin can be prepared in a range of equivalent weights from 1000 to 1800 to fit specific needs, and offers all the classic advantages of a solid catalyst in the ease of separation of products.

The choice of a solvent to use with Nafion-H is nontrivial. As stated, polar organic solvents are desired because they swell the resin. Acetic acid is useful but is not inert in the reactions studied here. Water and alcohols are found to decrease the activity of the catalyst when present in excess. Ethers such as glyme or diglyme were found not to be inert under reaction conditions, while THF is known to be polymerized over Nafion-H at room temperature.[4] However, p-dioxane was found to yield no GC-observable decomposition products when heated at 150° for 3 hours over the Nafion-H resin, and was used in most of the experiments reported here.

Carbonylation in the Presence of Water. With water present in the dioxane solvent, glycolic acid is presumably the product of formaldehyde carbonylation, as in equation 3. The most extensive series of experiments was done using these reactants. The series of experiments shown in Table I illustrates several aspects of this reaction. First, the reaction occurs readily under these conditions, giving routine yields of ca. 70% at 150°. The first two experiments may be compared to see that the reaction remains incomplete even after 3 hours at 130°, indicating a substantial temperature effect in this range. The series was run primarily to test the durability of the Nafion-H catalyst during these five reactions. The same Nafion-H catalyst was used in each of these reactions, and was only rinsed with dioxane and sucked dry on a filter between reactions. The yield of glycolic acid does indeed stay constant at 150°, with only a slight unexplained dip in the fourth reaction, indicating that the Nafion-H did maintain its catalytic activity through all the reactions. A different measure of this catalytic activity is the equivalent weight of the resin before and after the series. The initial equivalent weight was 1282 g/ equivalent, and afterwards was 1315 g/equivalent, a decrease in available acidity of less than three percent. This could conceivably be accounted for by washout of monomer during the first reaction.

A number of reactions were run in order to determine the effect of carbon monoxide pressure on the yield of glycolic acid in this system. The results are shown in Table II. With the other reaction conditions constant, the yield did increase from 50% to 80% upon increasing the pressure from 1500 psi to 4500 psi. While this does indicate that increasing the pressure of CO results in higher yields, the data should not be interpreted as showing that high pressures are required for high yields. The equipment used here was a rocking autoclave, and more efficient stirring may well enhance the efficiency of the reaction.

One reaction was done with a mixture of hydrogen and carbon monoxide to verify that the presence of hydrogen would have no effect on the yield. This run is also shown in Table II. The yield, 73%, is slightly higher than in comparable runs without hydrogen, but no significance is attached to this. In the presence

of this Nafion-H acid catalyst the hydrogen is expected to act only as a diluent, requiring proportionately higher total pressures to achieve the same carbon monoxide partial pressure as in the absence of the hydrogen.

The effect of water on the yield of glycolic acid in this reaction system was also explored. These data are shown in Table III-1. The amount of formaldehyde in these runs was reduced so that the initial mole ratio of water to Nafion-H could be varied and held approximately constant during a run, without being affected by the reaction. This molar ratio of water to Nafion-H was expected to change the effective acidity of the Nafion-H, which would in turn affect the yield in a given time. The reaction with the most water present, a 20:1 ratio of H_2O to H^+, did not result in complete conversion of the formaldehyde. Decreasing the ratio results in an optimum yield at a 5:1 ratio of water to acid. Decreasing the ratio still further to 2:1 and even 1:1 surprisingly results in a constant yield of about 50% glycolic acid (analyzed as methyl glycolate after conversion to the ester). Such yields in the presence of only half as much water as formaldehyde raise the question of whether glycolic acid is truly the reaction product, or whether dehydrated forms of glycolic acid such as the cyclic dimer glycolide, Figure 1a, or oligomers, Figure 1b, might not be the actual products.
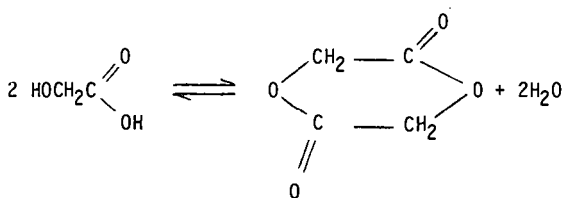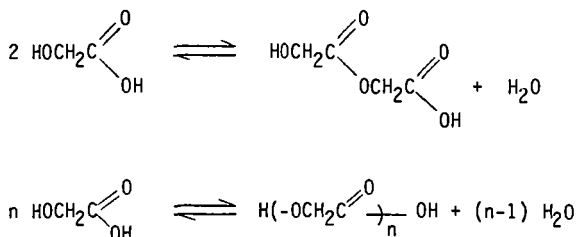

FIGURE 1a. Formation of Glycolide

FIGURE 1b. Formation of Glycolic Acid Oligomers

An indication that these dehydrated forms of glycolic acid are the actual products under these reaction conditions was gained from a semi-quantitative GC analysis of these reaction solutions for water. This analysis showed that all the water initially added to the reaction solution was still present in solution at the end of the reaction, and consequently could not be combined as glycolic acid. A reaction with no water added was included in an earlier series, shown in Table III-2. These three reactions also indicate that there is an optimum water to acid ratio, but a yield of even 25% with no water added is somewhat surprising. All these data demonstrate that too much water in the reaction solution reduces formaldehyde

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conversion and concomitantly glycolic acid yield, but the results at the lower levels of water are less definitive.

The preceding data show that in these reactions the conversion of formaldehyde is complete, or nearly so, while the yield of glycolic acid is always substantially less than quantitative. There are obviously by-products in this reaction. This subject has not been extensively investigated, but some comments on the suspected by-products and their mode of formation can be made.

The most likely side reaction is the acid-catalyzed reaction of formaldehyde with itself, instead of the desired acid-catalyzed reaction with carbon monoxide. One such reaction is the formation of methyl formate from formaldehyde,[6a] equation 10,
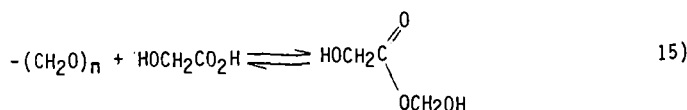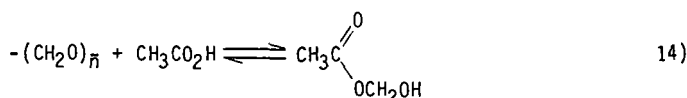
$$2 \ CH_2O \rightarrow HCO_2CH_3 \qquad\qquad 10)$$

but no evidence has been found to support this. Another possibility is the acid-catalyzed condensation of formaldehyde to polyhydroxy aldehydes, equation 11.

$$(n + 1) \ CH_2O \rightarrow H-[CH(OH)]_n-CHO \qquad\qquad 11)$$
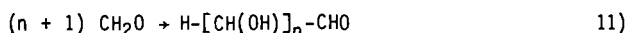
This reaction would be similar in stoichiometry to the formose reaction,[5] the base catalyzed condensation of formaldehyde to sugars and a mixture of polyhydroxy aldehydes. The solutions after reaction were varying shades of brown, and the Nafion-H sometimes turned a dark brown or even black, especially when the reaction contained little water or was exposed to high temperatures. This is reminiscent of the acid-catalyzed carbonization of sugars, equation 12.

$$H-[CH(OH)]_n-CHO \rightarrow (n + 1)C + (n + 1) \ H_2O \qquad\qquad 12)$$
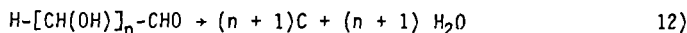
If these ideas about the nature of the byproducts are correct, then one approach to suppress the condensation of the formaldehyde would be to chemically separate the formaldehyde monomers with a solvent or an added component. The Nafion-H, as a strong acid, rapidly catalyzes polymerization of formaldehyde to polyoxymethylene (paraformaldehyde), and catalyzes the corresponding depolymerization at higher temperatures as well.[6a] Therefore, a reversible chemical interaction is needed to separate the formaldehyde monomers while permitting the carbonylation to proceed. Examples of such interactions to form unstable adducts are reaction with water, equation 13, to form methylene glycol;[6b] with acetic acid, equation 14), to form the unstable methylene glycol ester;[6c] and analogously with glycolic acid, equation 15.

$$-(CH_2O)_\overline{n} + H_2O \rightleftharpoons HOCH_2OH \qquad\qquad 13)$$

$$-(CH_2O)_\overline{n} + CH_3CO_2H \rightleftharpoons CH_3C\overset{\displaystyle O}{\underset{\displaystyle OCH_2OH}{\diagdown}} \qquad\qquad 14)$$

$$-(CH_2O)_n + HOCH_2CO_2H \rightleftharpoons HOCH_2C\overset{\displaystyle O}{\underset{\displaystyle OCH_2OH}{\diagdown}} \qquad\qquad 15)$$

Other investigators have disclosed the use of acetic acid as a solvent to yield acetylglycolic acid, equation 16, using a Nafion-H catalyst.[2] In the sulfuric

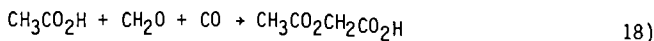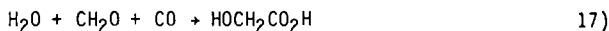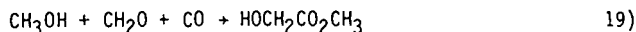$$CH_3CO_2H + CH_2O + CO \rightarrow CH_3CO_2CH_2CO_2H \quad 16)$$
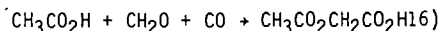
acid catalyzed reaction, glycolic acid has been disclosed as a useful solvent for enhancing yields.[7] However, data obtained in this study and shown in Tables IV-1 and IV-2 indicate that an equimolar amount of acetic acid has no effect in this reaction. In the absence of water the acetic acid actually decreases the yield. Glycolic acid, whether added wet or dehydrated, also decreases the yield of glycolic acid from formaldehyde. The reason for this decrease in yield is not readily apparent.

This Nafion-H catalyzed carbonylation of formaldehyde in dioxane/water has a number of aspects which make it an attractive intermediate reaction in a process for ethylene glycol preparation. A summary of these favorable aspects is as follows:

1. The Nafion-H solid acid catalyst is easily separated from the reaction products, a classic advantage of heterogeneous catalysts.

2. As demonstrated by others, solid acid resins similar to Nafion-H appear to be virtually non-corrosive.[2]

3. The catalyst is thermally stable, has shown no loss of activity with use, and is easily regenerable if necessary, e.g., due to contamination with other cations. Polar solvents swell the catalyst, which allows utilization of interior acid sites.

4. The acid catalyst retains its activity in the presence of substantial amounts of water; therefore, dry formaldehyde (as trioxane or paraformaldehyde) is not required.

5. The reaction is not affected by hydrogen, which acts only as a diluent for the carbon monoxide. The catalyst has no activity for the undesired reduction of formaldehyde to methanol. Consequently, synthesis gas could be used without separation or the carbon monoxide could be concentrated before use, and the separated hydrogen subsequently used for hydrogenolysis of the glycolic acid ester.

6. The reaction proceeds under reasonable conditions of temperature and pressure.

7. The glycolic acid product is stable to further reaction.

8. The dioxane solvent appears inert under reaction conditions.

Carbonylation in Ester Solvents. The acid-catalyzed carbonylation of formaldehyde has been carried out with water as discussed above, equation 17, with acetic acid, equation 18, and with methanol,[8],[9] equation 19.

$$H_2O + CH_2O + CO \rightarrow HOCH_2CO_2H \qquad\qquad 17)$$

$$CH_3CO_2H + CH_2O + CO \rightarrow CH_3CO_2CH_2CO_2H \qquad 18)$$

$$CH_3OH + CH_2O + CO \rightarrow HOCH_2CO_2CH_3 \qquad\qquad 19)$$

The reaction with acetic acid as solvent is reported to be efficient and specific, but the acetylglycolic acid product must be hydrolyzed and then esterified before it can be hydrogenated to ethylene glycol. The reaction with methanol as solvent would be ideal if it yielded only the methyl ester. However, substantial yields of alkoxy acids and their esters are also invariably produced in the presence of alcohols. These may be hydrogenated to glycol ethers, useful as solvents, but cannot serve as intermediates to ethylene glycol.

The reaction using an ester as solvent, e.g. methyl acetate in equation 20, appears not to have been reported before.

$$CH_3CO_2CH_3 + CH_2O + CO \rightarrow CH_3CO_2CH_2CO_2CH_3 \qquad\qquad 20)$$
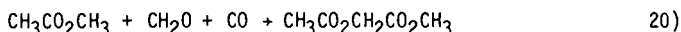
The product of the reaction with an ester, in this case methyl acetylglycolate, can be transesterified, e.g. with methanol as in equation 21 to yield methyl glycolate and regenerate methyl acetate.

$$CH_3CO_2CH_2CO_2CH_3 + CH_3OH \rightarrow CH_3CO_2CH_3 + HOCH_2CO_2CH_3 \qquad\qquad 21)$$
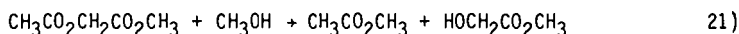
The methyl acetate can then be separated and the methyl glycolate hydrogenated to ethylene glycol.

Some formaldehyde carbonylations using methyl acetate as solvent are shown in Table V-1. It may be seen from the first reaction that the yield of methyl acetylglycolate, intermediate to ethylene glycol, is over 60%, but there is also some production of methyl methoxyacetate, 15% in this case. In the analysis of the reaction products from this run it was noted that some acetic acid was formed, presumably from the methyl acetate. The second reaction demonstrates that adding a small amount of acetic acid at the beginning of the reaction does not affect the yields of the two products. Addition of methanol at the beginning of the reaction has a profound effect, however, as shown in the third reaction. This may be because the formaldehyde is converted to methylal, $(MeO)_2CH_2$, by the added methanol. All the formaldehyde not accounted for in the products was recovered as methylal. Addition of water at the beginning of the reaction also decreases the yield of methyl acetylglycolate, and results in the formation of some free acids, notably methoxyacetic acid.

Methyl formate was also tested as an ester solvent, with typical results shown as the first reaction in Table V-2. The main reaction product expected here is methyl formylglycolate, $HCO_2CH_2CO_2CH_3$, but methyl glycolate, possibly derived from the former product by decarbonylation, is also found. Methyl methoxyacetate is formed in even greater yield than with methyl acetate as solvent.

A unique aspect of the reactions using methyl formate as solvent is that no CO pressure needs to be applied, as the second reaction in Table V-2 confirms. The methyl formate presumably acts as a source of CO, and the overall reaction in equation 22 results.

$$HCO_2CH_3 + CH_2O \rightarrow HOCH_2CO_2CH_3 \qquad\qquad 22)$$
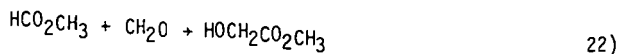
This reaction has been investigated by others using different strong acids.

The carbonylation of formaldehyde using Nafion-H resin does proceed in ester solvents, but not with complete selectivity to intermediates to ethylene glycol. The reaction might nevertheless be interesting as a means of coproducing ethylene glycol and glycol ethers.

Reactions of Methylal. In the preceding work using ester solvents the focus was on intermediates to ethylene glycol, avoiding the alkoxy esters or acids which can be produced as byproducts. These alkoxy esters or acids do have value, however, since they can be hydrogenated to glycol ethers, which are articles of commerce and are useful as solvents. Consequently, some reactions were run to determine if methylal could be carbonylated to methyl methoxyacetate efficiently and selectively over Nafion-H resin, as in equation 23.

$$CH_3OCH_2OCH_3 + CO \rightarrow CH_3OCH_2CO_2CH_3 \tag{23}$$
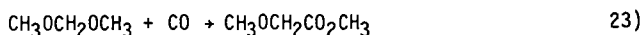
The results are shown in Table VI. The first reaction was carried out in dioxane solvent and resulted in only modest yields of both methyl methoxyacetate and methyl glycolate. Using a mixed methanol/dioxane (50:50) solvent resulted in no reaction at all. When methyl acetate was used as the solvent though, a good yield of both methyl methoxyacetate and methyl acetyl glycolate resulted; the former was not produced selectively.

There could be some question over whether methyl glycolate is inert to further reaction in this catalyst system, or if it can be methylated by the Nafion-H to form methyl methoxyacetate. One reaction was run in order to test this possibility. Methyl glycolate was reacted in a mixed methanol/dioxane solvent (10/40 by volume) over the Nafion-H resin using standard reaction conditions. No methyl methoxyacetate was found in the reaction solution, and the methyl glycolate was recovered quantitatively.
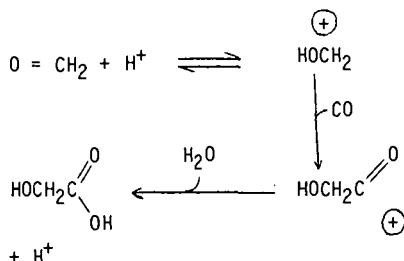
These results indicate that methylal can be carbonylated efficiently to methyl methoxyacetate, especially in ester solvents, but the reaction is not selective and results in substantial amounts of intermediates to ethylene glycol as well.

Aspects of the Mechanism. The acid-catalyzed reaction of formaldehyde with carbon monoxide belongs to the class known as Koch reactions.[10] The Koch reaction usually refers to the reaction of an olefin with carbon monoxide, as exemplified by the reaction of isobutene with CO and water, equation 24, to product pivalic acid.

$$\begin{array}{c} CH_3 \\ \diagdown \\ C = CH_2 + CO + H_2O \xrightarrow{H^+} (CH_3)_3CCO_2H \\ \diagup \\ CH_3 \end{array} \tag{24}$$
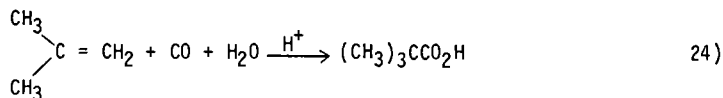
The first step in a Koch reaction is formation of a carbonium ion from the substrate and the acid catalyst. The carbonium ion then adds carbon monoxide to form a more stable acylium ion. This finally reacts with water to form the

free acid, or with an alcohol to form an ester. The reaction with formaldehyde
is:

$$O = CH_2 + H^+ \rightleftharpoons \overset{(+)}{HOCH_2}$$

$$\downarrow CO$$

$$HOCH_2C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup}} \xleftarrow{\quad H_2O \quad} HOCH_2C\overset{\displaystyle O}{\diagup} \quad (+)$$

$$+ H^+$$

The ease with which the Koch reaction takes place depends on how easily the sub-
strate is protonated. Protonation of formaldehyde requires a strong acid; some
data on the proton affinity of formaldehyde have been obtained.[11]

EXPERIMENTAL

        Materials: Glycolic acid was obtained as wet crystals (Aldrich) or 70%
aqueous solution (Pfaltz & Bauer). It was analyzed by titration with 0.1 M NaOH
using a phenolphthalein indicator. The "Nafion" 501 perfluorosulfonic acid resin
was obtained as a sample from the Plastic Products Division of DuPont. This
material consists of granules nominally 0.2 to 0.5 mm in diameter, and has an
equivalent weight of about 1200. It was received as the potassium sulfonate and
was converted to the acid form and analyzed essentially as recommended by
DuPont. Conversion to the acid form is achieved by soaking the resin about five
times in 4 M HCl, allowing time for exchange and with superficial washing with
distilled water between HCl treatments. This is followed by washing with
distilled water until the washings show a neutral pH, after which the material is
dried in a vacuum oven overnight at about 110°. The Nafion-H was stored in sealed
jars or in a desiccator as it can absorb appreciable amounts of water from the
air. Analysis of the acid form was carried out by soaking the resin in water with
an excess of sodium chloride, and titrating the liberated HCl with 0.1 M NaOH.
Dioxane was dried by refluxing over calcium hydride followed by distillation. All
other materials were reagent grade and used as received.

        Reactions: The reactions with carbon monoxide were carried out in a
300 cc rocking autoclave equipped with a glass liner, which contained 50 cc of
reaction solution over the Nafion-H. Carbon monoxide was introduced before
heating. The starting time of the reaction was taken as the time the autoclave
reached temperature (after approximately 30 minutes) and the autoclave was allowed
to cool and rock overnight after the heat was turned off at the end of the reac-
tion time. Formaldehyde was added as trioxane, the cyclic trimer; 8g, or ~6
mequiv Nafion-H was used in each run, and ~50 ml of p-dioxane was used as solvent.

        Analysis of Reaction Products: Analysis of the products was by gas
chromatography using peak area integration and a hexadecane internal standard.
Since glycolic acid gave poor sensitivity and reproducibility, this product was
analyzed as methyl glycolate by refluxing the entire reaction solution, including
the Nafion-H, with an excess of methanol before GC analysis. A semi-quantitative
estimate of the unreacted formaldehyde could be made through analysis of the
methylal resulting from reaction of methanol with the formaldehyde. These
analyses used a 6' x 1/8" Carbowax 20 M column, programming from 80° to 225° at

2°/min. A blank run, substituting a known amount of glycolic acid for formaldehyde, verified the utility of this analysis for glycolic acid. The reaction (mole ratios: glycolic acid, 10: water, 3.5: Nafion-H, 1; 150°, 3h, P_{CO} = 2500 psi)· resulted in analysis for 96% of the added glycolic acid. This result also indicates that the glycolic acid, once formed, is inert to further reaction under these conditions. This is in contrast to a catalyst system in which further carbonylation to malonic acid followed by decarboxylation to acetic acid proved to be a major problem.[12]

Preparations:

(1) Methyl glycolate, $HOCH_2CO_2CH_3$, (MG), was prepared by thermal reaction between dehydrated glycolic acid and excess methanol at 210° for 10 hours in a rocking autoclave.[13] The glycolic acid was dehydrated in a rotary evaporator by raising the temperature slowly to 180°.[13] Methyl glycolate was distilled under vacuum (22 mm, 61°) b.p. 150°, lit. 151.1°.[14a]

(2) Acetylglycolic acid, $CH_3CO_2CH_2CO_2H$, was prepared by heating dehydrated glycolic acid with excess acetic acid 10h at 200°. The product was recrystallized from ether/toluene. m.p. 63-65°; lit. 66-68°.[14b]

(3) Methyl acetylglycolate, $CH_3CO_2CH_2CO_2CH_3$, (MAG), was prepared by reaction of methyl glycolate with acetyl chloride in methyl acetate solvent. The product was distilled under vacuum; b.p. 82-83° at 22 mm.

(4) Methyl methoxyacetate, $CH_3OCH_2CO_2CH_3$, (MMAc), was prepared by refluxing commercially obtained methoxyacetic acid with an excess of methanol over Nafion-H and distilling the product; b.p. 128°, lit 131°.[14c]

ACKNOWLEDGMENTS

TABLE I

CARBONYLATION OF FORMALDEHYDE TO GLYCOLIC ACID
DURABILITY TEST USING THE SAME NAFION-H CATALYST[a]

Temperature	Time	P_{CO}	Unreacted Formaldehyde	Yield Glycolic Acid
130	3 h	2600	29%	38%
150	3 h	2700	5%	63%
150	5 h	2600	4%	68%
150	5 h	2700	6%	56%
150	5 h	2700	4%	69%

[a]Mole ratios: H_2O, 10: CH_2O, 10: H^+, 1.

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TABLE II

CARBONYLATION OF FORMALDEHYDE TO GLYCOLIC ACID.
DEPENDENCE OF YIELD ON CARBON MONOXIDE
PRESSURE, AND A REACTION IN THE PRESENCE OF HYDROGEN[a]

P_{CO} (psig)	Yield Glycolic Acid	Time
1500	48%	5 h
2500	61%	5 h
4600	79%	3 h
3000^{b}	73%	3 h

[a]Mole ratios: H_2O, 10: CH_2O, 10: H^+, 1; Temperature 150+°C.

[b]The gas used was 4000 psi of 25:75 H_2:CO.

TABLE III

CARBONYLATION OF FORMALDEHYDE TO GLYCOLIC ACID.
DEPENDENCE OF YIELD ON H_2O/H^+ RATIO[a]

	MOLE RATIOS			
	H_2O :	CH_2O :	H^+	Yield Glycolic Acid
1.	20	2	1	$36\%^{b}$
	10	2	1	44%
	5	2	1	57%
	2	2	1	49%
	1	2	1	48%
2.	20	10	1	61%
	10	10	1	72%
	0	10	1	25%

[a]Time, 3h; P_{CO}, 2500 psi; Temperature 150+°C

[b]Incomplete conversion

TABLE IV-1

EFFECT OF ADDED ACETIC ACID[a]

MOLE RATIOS

AcOH	:	H_2O	:	CH_2O	:	H^+	Yield Glycolic Acid
--		10		10		1	72%
10		--		10		1	40%
10		10		10		1	71%

[a]Time, 3h; Temperature, 150+°C; P_{CO}, 2500 psi

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TABLE IV-2

EFFECT OF ADDED GLYCOLIC ACID

Time	P_{CO}	Initial $HOCH_2CO_2H$	:	H_2O	:	CH_2O	:	H^+	Yield Glycolic Acid[a]
2 h	2500	11		4		12		1	40%
3 h	4000	12		(-8)[b]		10		1	13%

[a]Yield = (total yield - amount added)/moles CH_2O; Temperature, 150+°C

[b]The initial added glycolic acid was 66% dehydrated.

TABLE V-1

CARBONYLATION OF FORMALDEHYDE IN METHYL ACETATE[a]

$$CH_3CO_2Me + CH_2O + CO \rightarrow$$
$$CH_3CO_2CH_2CO_2Me \text{ (MAG) and } MeOCH_2CO_2Me \text{ (MMAc)}$$
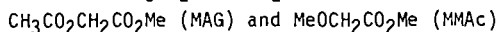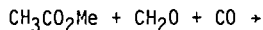
Added Component	Added Comp/CH_2O	%YIELDS		Notes
		MAG	MMAc	
--	--	61	15	b
Acetic Acid	1	63	13	
Methanol	2	18	23	c
Water	1	31	18	d

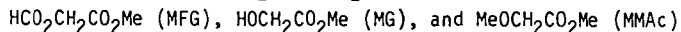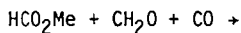[a]Time, 3h; Temperature, 150°; P_{CO}, 2500 psi; Mole ratios: CH_2O, 10: H^+, 1.

[b]Acetic acid found in reaction products.

[c]Methylal yield was 58%.

[d]Also substantial yields of methyl glycolate (18%) and methoxyacetic acid, $CH_3OCH_2CO_2H$. Time = 0.5 h.

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TABLE V-2

CARBONYLATION OF FORMALDEHYDE IN METHYL FORMATE

$$HCO_2Me + CH_2O + CO \rightarrow$$
$$HCO_2CH_2CO_2Me \text{ (MFG), } HOCH_2CO_2Me \text{ (MG), and } MeOCH_2CO_2Me \text{ (MMAc)}$$

% YIELDS			
MFG	MG	MMAc	Notes
11	11	31	a
5	17	21	b

[a]Temperature, 150°, P_{CO}, 2500 psi; Time 3h.

[b]No CO added, ΔP = +200 psi; Temperature, 150°; Time, 5h.

TABLE VI

CARBONYLATION OF METHYLAL TO
$MeOCH_2CO_2Me$ (MMAc), $HOCH_2CO_2Me$ (MG), and $CH_3CO_2CH_2CO_2Me$ (MAG)[a]

	% YIELDS		
Solvent	MMAc	MG	MAG
dioxane	20	17	not a product
methanol/dioxane, 50:50	0	0	not a product
methyl acetate	49	trace	39

[a]Time, 3h; Temperature 150°; P_{CO}, 2500 psi; Mole ratios: $(MeO)_2CH_2$, 10: H^+, 1.

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